

**METHOD #:** 410.4 Pending Approval for Sect. 304(h), CWA (Issued 1978)

**TITLE:** Chemical Oxygen Demand (Colorimetric, Automated; Manual)

**TITLE:** Chemical Oxygen Demand (Colorimetric, Automated; Manual)

**ANALYTE:** COD Chemical Oxygen Demand

**INSTRUMENTATION:** Spectrophotometer, Autoanalyzer

**STORET No.** 00340

## 1.0 Scope and Application

- 1.1 This method covers the determination of COD in surface waters, domestic and industrial wastes.
- 1.2 The applicable range of the automated method is 3-900 mg/L and the range of the manual method is 20 to 900 mg/L.

## 2.0 Summary of Method

- 2.1 Sample, blanks and standards in sealed tubes are heated in an oven or block digester in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digester, cooled and measured spectrophotometrically at 600 nm.

### 3.0 Sample Handling and Preservation

- 3.1 Collect the samples in glass bottles if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
- 3.2 Samples should be preserved with sulfuric acid to a pH < 2 and maintained at 4°C until analysis.

## 4.0 Interferences

- 4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.

## 5.0 Apparatus

- 5.1 Drying oven or block digester, 150°C
- 5.2 Corning culture tubes, 16 x 100 mm or 25 x 150 mm with Teflon lined screw cap
- 5.3 Spectrophotometer or Technicon AutoAnalyzer
- 5.4 Muffle furnace, 500°C.

## 6.0 Reagents

- 6.1 Digestion solution: Add 10.2 g  $K_2Cr_2O_7$ , 167 mL conc.  $H_2SO_4$  and 33.3 g  $HgSO_4$  to 500 mL of distilled water, cool and dilute to 1 liter.
- 6.2 Catalyst solution: Add 22 g  $Ag_2SO_4$  to a 4.09kg bottle of conc.  $H_2SO_4$ . Stir until dissolved.
- 6.3 Sampler wash solution: Add 500 mL of conc  $H_2SO_4$  to 500 mL of distilled water.
- 6.4 Stock potassium acid phthalate: Dissolve 0.850 g in 800 mL of distilled water and dilute to 1 liter. 1 mL = 1 mg COD
  - 6.4.1 Prepare a series of standard solutions that cover the expected sample concentrations by diluting appropriate volumes of the stock standard.

## 7.0 Procedure

- 7.1 Wash all culture tubes and screw caps with 20%  $H_2SO_4$  before their first use to prevent contamination. Trace contamination may be removed from the tubes by igniting them in a muffle oven at 500°C for 1 hour.
- 7.2 Automated
  - 7.2.1 Add 2.5 mL of sample to the 16 x 100 mm tubes.
  - 7.2.2 Add 1.5 mL of digestion solution (6.1) and mix.
  - 7.2.3 Add 3.5 mL of catalyst solution (6.2) carefully down the side of the culture tube.
  - 7.2.4 Cap tightly and shake to mix layers.
  - 7.2.5 Process standards and blanks exactly as the samples.
  - 7.2.6 Place in oven or block digester at 150°C for two hours.
  - 7.2.7 Cool, and place standards in sampler in order of decreasing concentration. Complete filling sampler tray with unknown samples.
  - 7.2.8 Measure color intensity on AutoAnalyzer at 600 nm.
- 7.3 Manual
  - 7.3.1 The following procedure may be used if a larger sample is desired or a spectrophotometer is used in place of an AutoAnalyzer.
  - 7.3.2 Add 10 mL of sample to 25 x 150 mm culture tube.
  - 7.3.3 Add 6 mL of digestion solution (6.1) and mix.
  - 7.3.4 Add 14 mL of catalyst solution (6.2) down the side of culture tube.
  - 7.3.5 Cap tightly and shake to mix layers.
  - 7.3.6 Place in oven or block digester at 150°C for 2 hours.
  - 7.3.7 Cool, allow any precipitate to settle and measure intensity in spectrophotometer at 600 nm. Use only optically matched culture tubes or a single cell for spectrophotometric measurement.

## 8.0 Calculation

- 8.1 Prepare a standard curve by plotting peak height or percent transmittance against known concentrations of standards.
- 8.2 Compute concentration of samples by comparing sample response to standard curve.

## 9.0 Precision and Accuracy

- 9.1 Precision and accuracy data are not available at this time.

## Bibliography

1. Jirka, A. M., and M. J. Carter, "Micro-Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand." *Anal. Chem.* 47:1397, (1975).

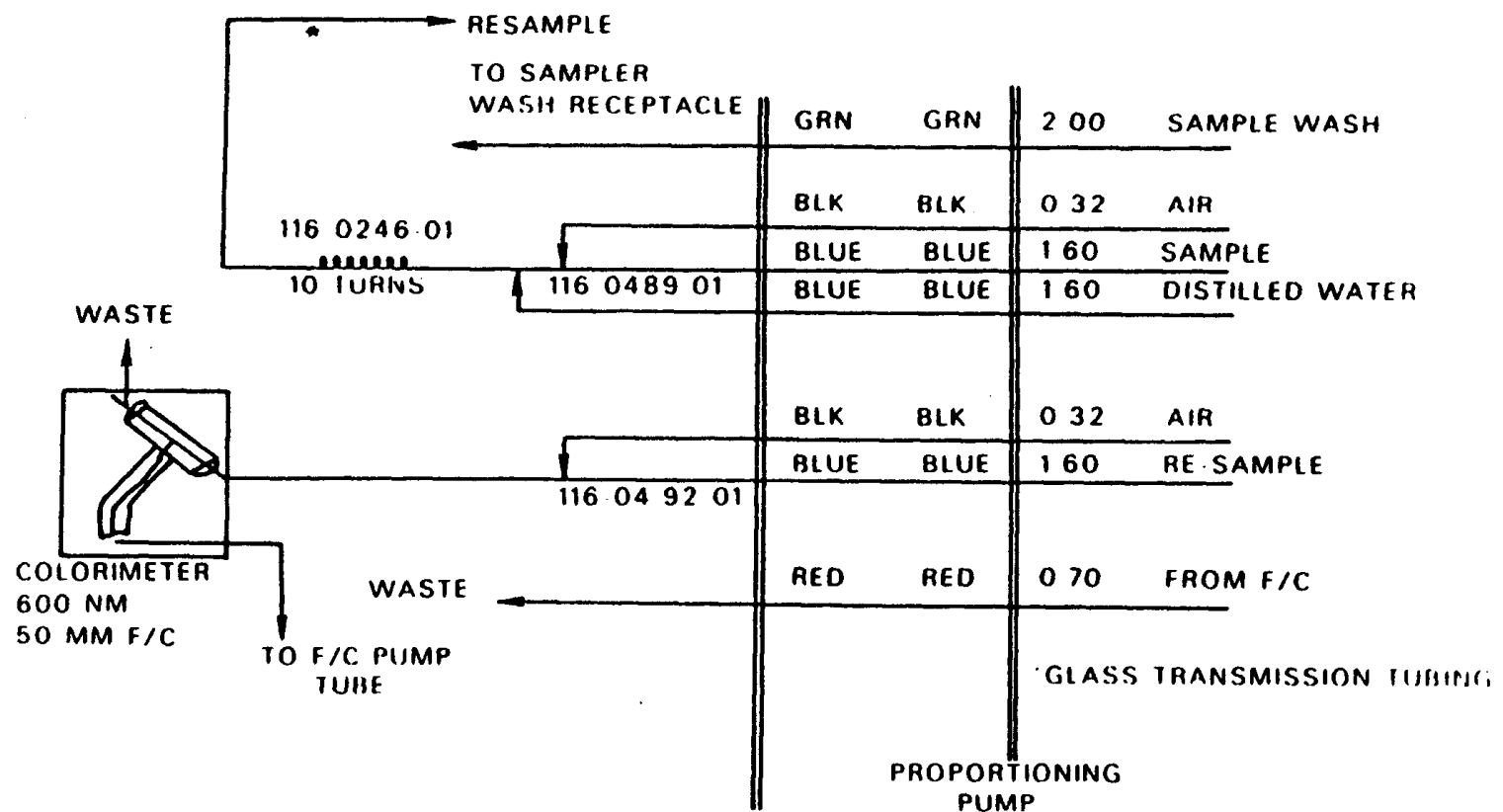


FIGURE 1 C O D MANIFOLD AA1 OR AA 11